NASA Technical Memorandum 81936

NASA-TM-81936 19810009673

RECENT DEVELOPMENTS IN POLYIMIDE ADHESIVES AT NASA-LANGLEY RESEARCH CENTER

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JANUARY 1981

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INTRODUCTION

High temperature adhesives have become increasingly important to NASA during the past five years for specific aerospace applications. These adhesive needs have developed in programs such as Composites for Advanced Space Transportation Systems (CASTS), Supersonic Cruise Research (SCR), and the Solar Sail. The CASTS program is directed towards the development of technology to decrease the structural weight of such vehicles as the Space Shuttle through the use of high temperature composites. The SCR program will help to select and develop materials for future supersonic transport structural applications. The NASA Solar Sail program is an outgrowth of the concept of solar wind propulsion in deep space. Vehicles and/or components for each of these programs have the common need for high temperature materials.

Adhesive bonding is a necessity for the advantages of high temperature fiber-reinforced, polymer-matrix, structural composites to be fully realized. The need for high temperature adhesives for these applications is heightened by the progress that has been made recently in the development of fabrication techniques for the production of high quality graphite/polyimide composites. The technology in high temperature adhesives is currently lagging the composite fabrication technology. Ultimately, the availability and reliability of high temperature adhesives will dictate the design, weight, and cost of these novel structural components.

At present, commercially available adhesives do not meet the requirements of the aforementioned programs. For this reason NASA-Langley Research Center undertook a research program to develop high temperature adhesives. Aromatic polyimides were chosen as a logical system to investigate because of their known thermal stability. This research program has encompassed both linear and addition polyimides.

LINEAR POLYIMIDE ADHESIVE DEVELOPMENT

Solvent Studies

Historically, it has been axiomatic that adhesives prepared from linear aromatic polyimides must be processed in the amide-acid form because once they have been imidized they become intractable (Figure 1).

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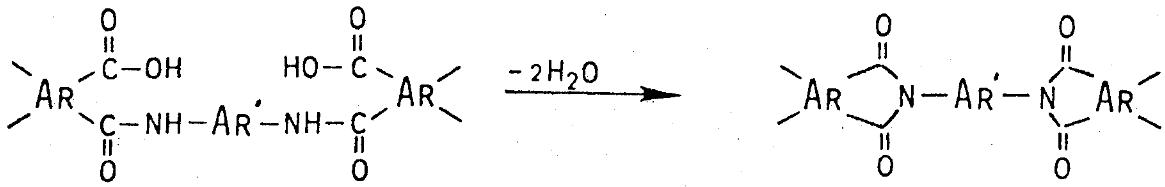
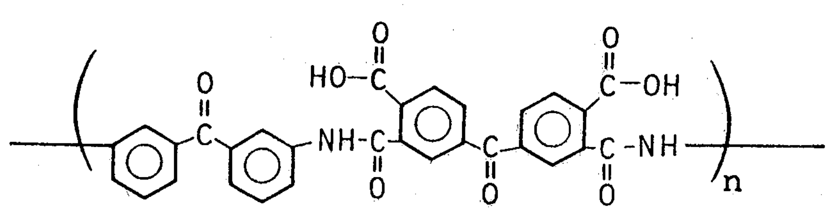


Imidization Step

Figure 1

The early polyimide adhesives (Ref. 1) were prepared as the amide acid, generally in a highly polar solvent such as N,N-dimethylacetamide (DMAc) or N,N'-dimethylformamide (DMF). These amide solvents tended to be retained by the polymer during bonding, not only causing voids but actually promoting degradation of the adhesive through transamidization (amide acid interacting chemically with the amide solvent). In order to overcome this deficiency with amide solvents an investigation was begun to find more suitable solvents to better utilize polyimides as adhesives.

A long list of solvents was screened using a polyimide system, LaRC-2 (ref. 2) which had earlier been shown in our laboratory to have good adhesion to glass (Figure 2).



LARC-2 Adhesive

Figure 2

LaRC-2 prepared in DMAc or DMF was a high molecular weight polymer. When films were made by casting a layer of the polymer onto plate glass followed by a thermal treatment to 300°C, they remained flexible. However, a darkening of these films seemed to indicate polymer degradation. Most other solvents that would yield high molecular polymer also resulted in this darkening of films during thermal conversion of the polyamide acid to the polyimide.

One series of solvents did permit the polymers to build to high molecular weight and seemed to cause very little discoloration during the thermal conversion. These were the aliphatic ethers. Simple ethers such as diethyl ether did not dissolve the monomers, but tetrahydrofuran (THF), dioxane and diglyme were good solvents for both the monomers and the resulting polyamide acid. Not only did these ether solvents seem to chemically interact less with the polymer, but the diglyme yielded a remarkable increase in adhesive strength as illustrated in Table 1 (Ref. 2).

TABLE 1

LARC-2 Polyimide Adhesive Strength in Various Solvents

Solvent	Lap Shear Strength, psi (MPa)*
Dimethylformamide (DMF)	500 (3.5)
Dimethylacetamide (DMAc)	2500 (17)
DMAc/Dioxane	2900 (20)
Diglyme	6000 (41)

* Titanium Adherends; RT Test

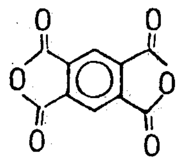
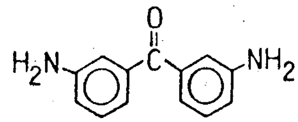
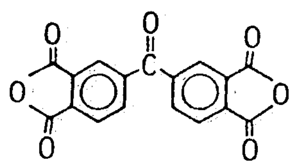
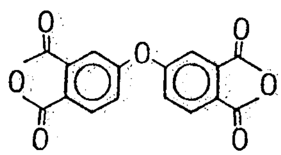
Diglyme is in general use today as a solvent for several polyimide adhesive systems.

Structure-Property Relationships

With diglyme as the solvent a series of polyimides was screened for potential use as adhesives (ref. 3). A general trend was found that a flexibilizing group between the benzene rings in the anhydride portion of the polymer increased adhesive strength as shown in Table 2.

TABLE 2

Effect of Anhydride on Adhesive Strength

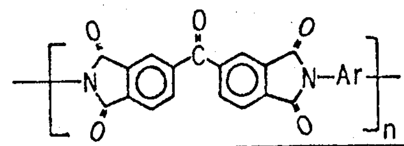
Anhydride	Amine	Lap Shear Strength, psi (MPa)*
		0 (0)
	"	6000 (41)
	"	4700 (32)

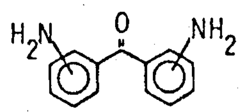
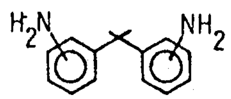
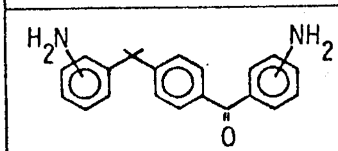
* Titanium Adherends; RT Test

In order to assess the effect of the amine on adhesive strength, several variations were made and are reported in reference 3. The major finding was that when the amino group was on the benzene ring in a position <u>meta</u> (3-position) to the group that links the rings, the strengths were always considerably higher than for the corresponding <u>para</u> (4-position) system. These data are presented in Table 3.

TABLE 3

Amine Isomer Effect In Linear Polyimides



AMINE STRUCTURE (Ar)	AMINE ISOMER	LAP SHEAR STRENGTH,* psi (MPa)
	3,3'	6000 (41)
	3,4'	2500 (17)
	4,4'	2600 (18)
	3,3'	4200 (30)
	4,4'	1900 (13)
	3,3''	4200 (30)
	4,4''	2600 (18)

*TITANIUM ADHERENDS ; RT Test

A Thermoplastic Polyimide

An important observation resulted from the amine isomer study. The polyimide based on the BTDA and 3,3'-diaminobenzophenone recently has been found to be a true thermoplastic when in the imide form. This thermoplastic nature is undoubtedly due to the flexibility introduced by the bridging groups in both the dianhydride and the diamine. The amine linkage being through the meta position also seems to enhance the thermoplastic nature (ref. 4). This thermoplastic polyimide has been designated LaRC-TPI (Thermoplastic Imide). Presently this polyimide has considerable potential as an adhesive (ref. 5). Void free bonds can be obtained because of its thermoplastic flow. As an adhesive for titanium it retains useful properties at 232°C after thousands of hours exposure (Table 4).

TABLE 4

LARC-TPI Adhesive Properties

Test Temperature, °C	Lap Shear Strength, psi (MPa)*
25 (Initial)	5300 (37)
232 (Initial)	1900 (13)
232 (After 1000 hrs. @ 232)	2500 (17)
232 (After 3000 hrs. @ 232)	3000 (21)

* Titanium Adherends

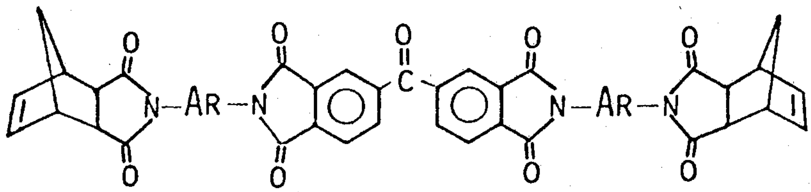
LaRC-TPI also shows considerable potential for use as an adhesive for bonding or laminating polyimide films such as Kapton (Du Pont's registered tradename)*. This potential is becoming increasingly important in flexible electronic circuitry. When Kapton films are laminated to each other or to metal foils using LaRC-TPI, the bond does not fail when subjected to a standard peel test; the Kapton films fail. Since LaRC-TPI is a thermoplastic, large area adhesive bonds can be fabricated with no voids in them. These laminated circuits (Kapton/copper/Kapton) have been able to withstand a ten second immersion in a molten solder bath without blistering or delaminating.

This ability to form large-area, void-free bondlines is a first for fully aromatic polyimides and makes LaRC-TPI a leading candidate for future structural bonding in NASA programs such as CASTS and SCR. LaRC-TPI is presently in its first stages of commercialization and may be marketed commercially through a licensing agreement with NASA.

ADDITION POLYIMIDE ADHESIVE DEVELOPMENT

Structure-Property Relationships

Adhesives prepared from linear aromatic polyimides classically exhibited low flow and gave off volatiles during their cure. These two major problems made linear polyimides unsuitable for structural adhesive applications in the aerospace industry. An innovation was made in the early 1970's when short-chain, amine-terminated aromatic polyimides were endcapped with 5-norbornene-2,3-dicarboxylic anhydride (nadic) as in Figure 3.

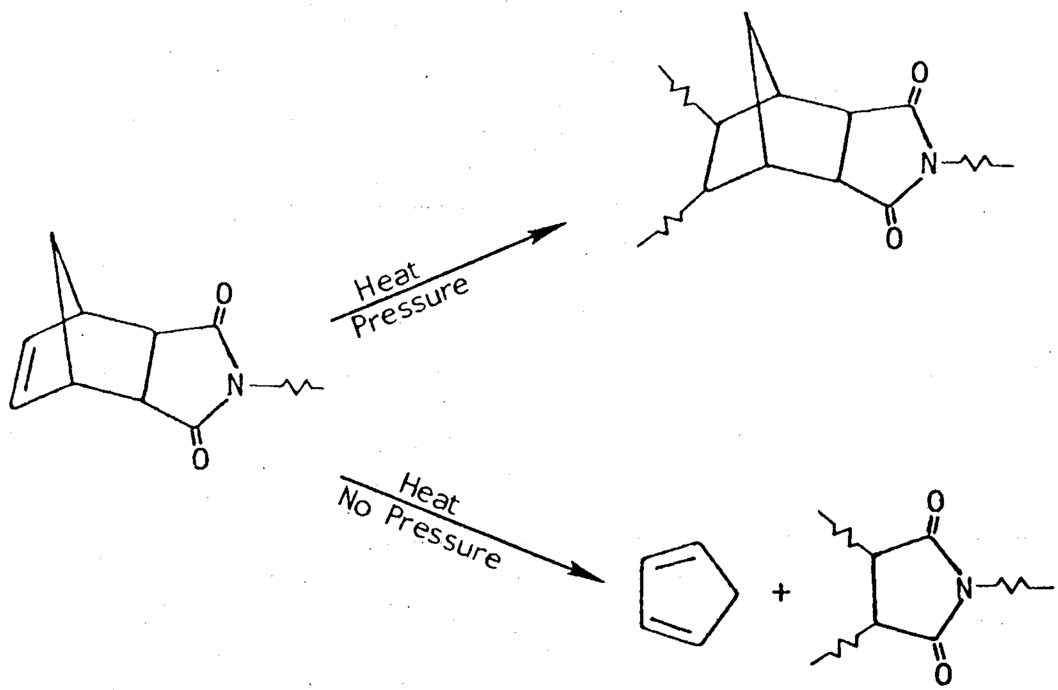


Nadic Terminated Imide

Figure 3

*Use of tradenames should not be taken as an endorsement by NASA of a commercial product.

This short-chain polymer (oligomer) had adequate flow upon heating to allow for more facile processing than with the linear systems (ref. 6). This system was a thermoset since crosslinking occurred through the unsaturated nadic endcaps. An added bonus with this system was that no volatiles were generated after the removal of the solvent because the fully imidized system retained enough flow for processing. However, if the cure of these systems with nadic endgroups is not carried out under pressure, the nadic portion of the molecule tends to dissociate into two components. One is a volatile chemical, cyclopentadiene. In both situations the polymer crosslinks or cures, but the evolution of cyclopentadiene can be detrimental, especially for adhesive applications (Figure 4).



Cure of the Nadic Capped Imides

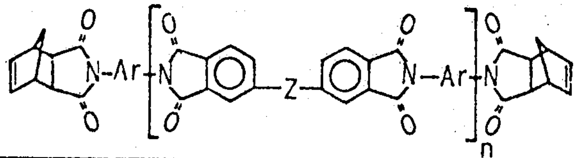
Figure 4

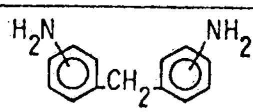
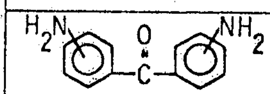
The first nadic endcapped polyimides were readily processable but did not perform well for adhesive applications. In order

to develop a good nadic capped adhesive system NASA-Langley began a structure-property relationship study to determine what chemical structures would provide useable adhesives for aerospace components (ref. 7). The adhesive data on several of these systems are shown in Table 5.

TABLE 5

Structure/Adhesive Property Relationships in Nadimides



AMINE STRUCTURE (Ar)	Z	AMINE ISOMER	LAP SHEAR STRENGTH,* psi (MPa)
	$-\underset{O}{\underset{\|}{C}}-$	3,3'	2800 (19)
	$-\underset{O}{\underset{\|}{C}}-$	4,4'	600 (4)
	-O-	3,3'	2500 (17)
	-O-	4,4'	1300 (9)
	$-\underset{O}{\underset{\|}{C}}-$	3,3'	2100 (14)
	$-\underset{O}{\underset{\|}{C}}-$	4,4'	1300 (9)
	-O-	3,3'	3000 (21)
	-O-	4,4'	1300 (9)

*TITANIUM ADHERENDS; RT Test

The commercially available material (second in the table) had the poorest lap shear strength of any of the systems tested. Again, just as in the linear polyimide adhesive study, the meta (3-position) linked diamine systems were the best adhesives. The first material in Table 5 has been designated LaRC-13 and has been used for several specialized applications in both the CASTS and SCR programs. A major advantage of this material is its high degree of flow during cure. Also, because of its high crosslink density LaRC-13 can be used well in excess of its glass transition temperature (270°C). This adhesive was successfully used to bond a high temperature composite to a ceramic for a missile application which required the adhesive to perform for several seconds at 595°C. CASTS application criteria of adequate adhesive strength after 125 hours at 316°C were successfully met by LaRC-13.

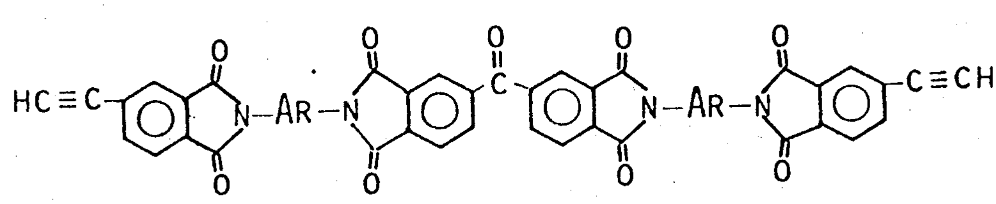
The major usage of LaRC-13 has been for the fabrication of honeycomb sandwich structures. The adhesive requirements for this application are a system that will bond at low pressure (345 kPa, 50 psi), because the honeycomb can collapse at higher pressures, and one which tends to fillet around the cell structure. LaRC-13 meets both of these requirements.

Toughening

Generally, all highly crosslinked adhesives have a low resistance to peel forces. This is not considered to be a serious deficiency for rigid honeycomb structure or similar applications where these forces are not encountered. However, a serious consideration in aerospace structures is their resistance to impact damage. The impact properties of adhesives is generally considered to be directly proportional to their peel properties. A recent program at NASA-Langley was directed toward the toughening of LaRC-13 so that its versatility could be enhanced (ref. 8). The approach was to incorporate elastomers into the adhesive which would act as energy absorbers. Several elastomers were successfully incorporated into the adhesive, and increases in room temperature peel strengths of nearly eightfold were realized.

Thermal Stability

Although nadic endcapped polyimides offer considerable advantages in processing, they do suffer from poor thermo-oxidative stability. Because the nadic caps are aliphatic in nature, they cannot withstand elevated temperatures in air without gradually burning up. Recent work by others (ref. 9) has shown the use of different crosslinking endcaps may lead to more thermo-oxidatively stable, thermoset imides. The most promising endcap of this type at present is the ethyne or acetylene group as shown in Figure 5.



Acetylene Terminated Imide
(ATI)

Figure 5

Originally it was postulated that the cure of this type system would yield a completely aromatic network through the trimerization of the acetylene groups to form benezene rings. However, more recent work has shown this cure to proceed to a highly conjugated system which is also very thermo-oxidatively stable (ref. 10).

In order to improve on LaRC-13, NASA-Langley investigated the use of the same basic chemical formulation with the only change being the 4-ethynylphthalic anhydride used in place of the nadic anhydride (ref. 11). The adhesive that was generated had the structure in Figure 5 where the Ar group was the 3,3'-diaminodiphenylmethane (same as for LaRC-13). This ATI material was compared to LaRC-13 for adhesive properties and the results are in Table 6.

TABLE 6

Comparison of Acetylene Terminated Imide (ATI) to LARC-13

	Lap Shear Strength, psi (MPa)*			
	Initial		After 1000 hrs. @232°C	
Adhesive	25°C	232°C	25°C	232°C
LARC-13	3200 (22)	2600 (18)	2600 (18)	1950 (13.5)
ATI	2900 (20)	2500 (17)	2500 (17)	2800 (19)

* Titanium Adherends

The initial lap-shear strengths of both adhesives are very similar at room temperature and at 232°C. However after exposure at 232°C for 1000 hours in an air-circulating oven the LaRC-13 samples were beginning to show signs of oxidation and this was reflected in a loss of 25 percent in strength when tested at 232°C. The ATI, conversely, gained 12 percent. The slight loss in room temperature strengths after aging for both systems was expected due to continued crosslinking. These data show the ATI system to have much better retention of initial strength and

that LaRC-13 is beginning to degrade and may have only limited utility for exposures beyond 1000 hours at 232°C. The exposure limit at 232°C for the ATI has not yet been determined.

SUMMARY

High temperature adhesives are becoming increasingly important for aerospace applications. Presently there are few commercially available high temperature adhesives and those that are available do not meet the stringent needs of specific aerospace programs. Polymer researchers at NASA-Langley Research Center have developed several novel polyimide adhesives to fulfill these needs. These adhesives have resulted from programs in basic research in the area of aromatic polyimides. These programs have been based on structure-property relationships of both linear and addition aromatic polyimides.

The work in linear polyimides has progressed to the development of a thermoplastic polyimide, LaRC-TPI, which is in its initial stages of commercialization. This material shows promise for general adhesive applications in aerospace structural components and appears to have potential for specialty applications such as the laminating of high temperature flexible electronic circuits.

The addition polyimide systems show potential for short-term elevated temperature uses up to 595°C. These adhesives are not as thermo-oxidatively stable as the linear systems and are more brittle, but these deficiencies are offset by their facile processing. Recent work has shown that these addition systems can be toughened and made more thermo-oxidatively stable through chemical modifications.

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1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
TM-81936		

4. Title and Subtitle	5. Report Date
RECENT DEVELOPMENTS IN POLYIMIDE ADHESIVES AT NASA-LANGLEY RESEARCH CENTER	January 1981
	6. Performing Organization Code
7. Author(s)	8. Performing Organization Report No.
Terry L. St. Clair	
9. Performing Organization Name and Address	10. Work Unit No.
NASA Langley Research Center Hampton, VA 23665	505-33-33-02
	11. Contract or Grant No.
12. Sponsoring Agency Name and Address	13. Type of Report and Period Covered
National Aeronautics & Space Adminstration Washington, DC 20546	Technical Memorandum
	14. Sponsoring Agency Code

15. Supplementary Notes Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Adminstration.

16. Abstract

Adhesive development at NASA-Langley has been primarily directed towards elevated temperature applications (200-300°C). Because of thermal stability considerations, the most attractive adhesives for this temperature range are linear and addition polyimides.

The linear polyimide adhesive research has encompassed basic structure-property relationships, solvent studies and formulations to meet various requirements. The most recent research in linear polyimide systems has been in the development of thermoplastic systems in an effort to eliminate the undesirable evolution of water classically associated with the cure going through an amide-acid intermediate step in the cure process. Commercialization of one of these thermoplastic adhesives, LaRC-TPI, is underway.

Addition polyimide adhesive research was also undertaken in order to avoid water evolution during cure. Basic structure-property relationships for these materials led to an adhesive which has been used extensively for high temperature adhesive needs within NASA and at several aerospace companies. Since addition systems are of a highly crosslinked nature, they are not as resistant to impact as their linear counterparts. In order to overcome this problem, research has been done in the area of elastomer-toughening these polymers. Work at NASA-Langley has also been concerned with the development of a crosslinking (or end cap) group which will lead to final products with thermal stabilities comparable to the linear systems.

These areas of linear and addition polyimide research will be discussed in sufficient detail to illustrate the progression of adhesive development at NASA-Langley Research Center during the past decade.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Polyimide Adhesive High temperature adhesive Structural adhesive	Unclassified-unlimited Subject category 27

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	12	A02

N-305 For sale by the National Technical Information Service, Springfield, Virginia 22161